CHAPTER 1

Mole Concept and Reaction Stoichiometry

Introduction

The quantitative aspects of **Chemical Equations** are crucially important. How much reactants you need to produce a given amount of product through a chemical reaction? How much fuel is needed to get to a specified destination? How much sulphur does a company have to mine to produce one million tons of sulphuric acid? How many calories do you need for lunch in order to run five miles? Chemical reactions are everywhere. In order to answer all these questions, a systematic, stepwise approach is required. Besides these common questions regarding stoichiometry, it is the first step towards answering questions related to any part of physical chemistry. In a nutshell, stoichiometry is in the every breath of entire physical and analytical chemistry. In this chapter, we will develop the full power of the **"Mole Concept, and Reaction Stoichiometry."** — the 'master key' to understand the analysis of molecules and chemical reactions.

Learning Signposts

- The mole
- Atom and related weight calculations
- Molecules and the molecular theory of matter
- Laws of chemical combination
- Empirical formula and its determination
- Calculations based on chemical equations
- Measuring strength of a solution
- Calculating weight of the solute, and volume of a solution

Reaction Stoichiometry as a 'Recipe'

A chemical equation for a reaction is essentially a recipe. Our purpose is to ground the rather abstract notions of chemical formulas and equations to something concrete. All of the quantitative aspects of any class of chemical equations — collectively known, as *reaction stoichiometry*—can be understood in terms of recipe concepts (*to make fruit salad for a party*) described below :

Fruit Salad Recipe : You intend to make 25 fruit salads servings for a dinner party according to the following recipe:

1.00 Apple + 4.00 Orange + 12.00 Grapes

Now you go to the store to purchase starting materials and come home with 5.00 kg apples, 8.00 kg of oranges and 0.50 kg of grapes. Are these materials sufficient to make 25 fruit salad servings?

To answer this question, the information available is insufficient. The reason being, your recipe for one fruit salad is expressed in numbers and you have them with the information of their weights. Clearly you need more information, specifically, the average mass of an apple, an orange and a grape. Suppose you have weighed a typical apple, orange and grape separately. Suppose further that the apples, oranges and grapes are unusually uniform in size and weight, so that the weight of one apple faithfully represents the weight of any apple and it is true for oranges and grapes. Suppose your weighing gives the results as shown in *Table* 1.1.

Table 1.1

Fruits	Apple	Orange	Grapes
Weight	$\frac{1}{8}$ kg	$\frac{1}{6}$ kg	$\frac{1}{6} \times 10^{-3}$ kg
No. of fruits available	40	48	3000

Now for 25 fruit salads, you need 25 apples, 100 oranges and 300 grapes. Apples and grapes are more than enough to produce 25 fruit salad but orange are less than the requirement. We can conclude that the number of oranges that you have at hand will limit the number of fruit salad servings. Because you need four orange per fruit salad, you can make only 12.00 fruit salads from 48 oranges. This will require 12 apples and 144 grapes. Specifically, you will require 13 × 4 = 52 oranges for 13 more fruit salads.

From the above example, we get a few important ideas. First, the recipe is expressed in numbers of units of each ingredient, not in terms of their masses. Second, the amount of fruit salad ingredients is expressed as mass which you buy them at the stores. Similarly, when we buy chemicals, the amounts are expressed as their masses. Third, to apply the recipe, we must convert the masses to the number of items using the mass of a single item. Having done this we figure out how many fruit salads is possible to make with the given amount of ingredients. Some of the ingredients may be less than the requirement and that limits the amount of products to be formed, no matter how large are the amounts of other ingredient available. In this typical fruit salad example, the number of fruit salads that could be formed (only 12) was limited due to limited amounts of oranges. We do the same thing with chemical equation. In many cases, one of the reactants limits the amount of product that can be formed in a chemical reaction. This will be the reactant that will be used up first, and it is known as the ***"Limiting Reagent"***.

The Mole

Mole is the unit chemists use to keep track of large numbers of atoms, ions and molecules. The unit was invented to provide a simple way of reporting the huge numbers – "the massive heaps"— of atoms and molecules in visible samples.

One mole is the number of atoms in exactly 12 g of carbon-12 isotope. With the help of mass-spectrometry, mass of an atom of carbon-12 isotope was found to be 1.9926×10^{-23} g. It follows that the number of atoms in exactly 12 g of carbon-12 is

Number of carbon-12 atoms

$$= \frac{12\text{ g}}{1.9926 \times 10^{-23}} = 6.023 \times 10^{-23}$$

Because mole gives the number of atoms in a sample, it follows that 1.00 mole of any element contains 6.023×10^{23} atoms of that element. This number (6.023×10^{23}) is known as ***Avogadro number*** (N_A).

Intext Q. 1 *Predict qualitatively about the 'idea' of Avogadro number had the C-14 scale been chosen in place of C-12.*

Answer C-14 atom is heavier than C-12 atom, thus in 12 g of C-14, the number of atoms would be less than the same in 12 g of C-12 isotope. Therefore, value of Avogadro number would be less on C-14 scale.

Instance 1 *A sample of vitamin C is known to contain 1.29×10^{24} hydrogen atoms and 2.58×10^{24} oxygen atoms. How many moles of hydrogen and oxygen atoms are present in the sample?*

Explanation Number of moles of H atom

$$= \text{Number of H atoms}/\ N_A$$

$$= \frac{1.29 \times 10^{24}}{6.023 \times 10^{23}} = 2.14 \text{ mole}$$

Number of moles of O atom

$$= \text{Number of oxygen atoms}/N_A$$

$$= \frac{2.58 \times 10^{24}}{6.023 \times 10^{23}} = 4.28 \text{ mole}$$

Atom and Related Weight Calculations

According to Dalton's atomic theory, "an atom is the smallest unit of which all matter is composed. It takes part in chemical reactions and it is indivisible in such reactions.

Atomic mass/Atomic weight

As the single atom of an element is a very small particle, absolute measurement of mass of a single atom is very difficult. In order to overcome this difficulty, scales of relative atomic masses were thought off. On the basis of these relative scales, relative heaviness of an element with respect to the weight of an atom of some standard element were proposed. Therefore, on relative scale, "Atomic weight" were defined as

Atomic weight

$$= \frac{\text{Weight of an atom of any element}}{\text{Standard weight}}$$

Some Older Scales of Atomic Weight

The first scale proposed for this purpose considered hydrogen atom as standard and mass of an atom of hydrogen were considered to be the standard weight.

On hydrogen scale, atomic weight of an element was defined as the number which indicates that how many times an atom of that element is heavier than an atom of hydrogen.

$\therefore$ Atomic weight (A)

$$= \frac{\text{Weight of one atom of the element}}{\text{Weight of one hydrogen atom}}$$

Later, the hydrogen scale was abandoned on account of the following limitations with hydrogen and a new scale with oxygen as standard element was proposed :

(i) Hydrogen being the lightiest element, precise measurement of weight of one atom of hydrogen is very difficult.

(ii) Oxygen is more reactive than hydrogen, therefore is easier to obtain compounds of an element with oxygen than with hydrogen.

(iii) Atomic weights of elements calculated on the basis of oxygen scale were found to be mostly whole numbers.

On oxygen scale, atomic weight of an element was defined as

Atomic weight of an element

$$= \frac{\text{Weight of one atom of the element}}{\frac{1}{16^{\text{th}}}\text{ Part by weight of an atom of O-16 isotope}}$$

$$= \frac{\text{Weight of one atom of the element}}{\text{Weight of an atom of O-16 – isotope}} \times 16$$

The IUPAC scale

According to the latest convention of IUPAC, an atom of C-12-isotope with its mass number of 12, has been accepted as the standard and the atomic weight of an element defined as

Atomic weight of an element

$$= \frac{\text{Weight of one atom of an element}}{\frac{1}{12^{\text{th}}}\text{ part by weight of an atom of C-12 isotope}}$$

$$= \frac{\text{Weight of one atom of an element}}{\text{Weight of one atom of a C-12 isotope}} \times 12$$

Therefore, on the basis of present C-12 scale, atomic weight of an element is a number which indicates that one atom of the said element is how many atomic weight times heavier than $1/12^{\text{th}}$ part by weight of an atom of C-12 isotope.

The standard weight, which is $1/12^{\text{th}}$ part by weight of one atom of C-12 isotope is known as "Atomic Mass Unit" or simply "amu" or "u". Earlier, we defined Avogadro number as number of atoms in exactly 12.00 g of C-12 isotope.

$$\Rightarrow \text{Weight of one C-12 atom} = \frac{12.00}{N_A}\text{ g}$$

$$\Rightarrow \text{One amu} = \frac{1}{12.00} \times \frac{12.00}{N_A}\text{ g}$$

$$= \frac{1}{6.023 \times 10^{23}} = 1.66 \times 10^{-24}\text{ g}$$

Therefore, atomic weight (A) can be redefined in terms of "amu" as:

$$A = \frac{\text{Weight of one atom of the element}}{\text{amu weight}}$$

Atomic weight calculated for some of the common elements on amu scale are tabulated below:

Table 1.2 Some atomic weights on amu scale

Elements	Atomic Weight	Elements	Atomic Weight
Hydrogen (H)	1.008 u	Barium (Ba)	137.3 u
Oxygen (O)	16.00 u	Fluorine (F)	19 u
Chlorine (Cl)	35.45 u	Gold (Au)	197 u
Iron (Fe)	55.85 u	Lead (Pb)	207.2 u
Sodium (Na)	23.00 u	Tin (Sn)	118.7 u

On the basis of above atomic weight table, it can be concluded that:

One atom of hydrogen is 1.008 times heavier than an u.

One atom of oxygen is 16 times heavier than an u.

One atom of iron is 55.85 times heavier than an u, and so on.......................... .

Knowing the atomic weight of an element, the absolute weight of an atom of that element can be determined as

$$\begin{pmatrix}\text{Absolute weight of one}\\ \text{atom of an element}\end{pmatrix}$$

$$= \text{Atomic weight} \times u$$

$$= \text{Atomic weight} \times 1.66 \times 10^{-24} \text{ g}$$

Absolute mass of one hydrogen atom

$$= 1.008 \times 1.66 \times 10^{-24} \text{ g}$$

$$= 1.67328 \times 10^{-24} \text{ g}$$

Absolute mass of one chlorine atom

$$= 35.45 \times 1.66 \times 10^{-24} \text{ g}$$

$$= 5.8847 \times 10^{-23} \text{ g}$$

Absolute mass of one sodium atom

$$= 23 \times 1.66 \times 10^{-24} \text{ g}$$

$$= 3.818 \times 10^{-23} \text{ g}$$

Important Points Regarding Atomic Weight

(i) It is a relative weight of an atom, not be absolute one.

(ii) It is a ratio of weights, therefore it has no unit, it is a simple number.

(iii) It allow us to express weight of an atom of any element in simple numerical form as compared to the tedious numerical values of absolute atomic weight of any element.

(iv) It allow us the conversion of atomic weight into absolute atomic weight in a simple manner as

Absolute atomic weight = Relative atomic weight × "amu" weight.

Intext Q. 1 *What quantities are needed for determining absolute weight of one atom of any element?*

Answer Atomic weight, and weight of one amu.

Absolute atomic weight = Atomic weight × amu weight

The gram atomic weight or "Molar Mass"

Gram atomic weight also known as molar mass of an element is defined as weight of Avogadro's Numbers (1.00 mole) of atom of that element in gram unit.

⇒ Gram atomic weigh "M"=Weight of one atom in gram unit × (N_A) Avogadro's Number.

∵ Weight of one atom = Atomic Weight × u weight

⇒ M = Atomic weight×u×Avogadro's Number gram.

⇒ = Atomic Weight×1.00 g

= Atomic Weight in gram unit.

$$\left[u \times \text{Avogadro's Number} = \frac{1}{N_A} \times N_A \text{ g} = 1.00 \text{ g}\right]$$

Therefore, molar mass of any element is numerically equal to its atomic weight expressed in gram unit and it represents the absolute mass of 1.00 mole of atoms of this element.

Molar mass of Na is 23g it indicates that 6.023×10^{23} atoms of Na metal weigh 23 g on absolute scale.

Intext Q. 1 *Why atomic weight and molar mass of an element are numerically the same?*

Answer One mole of u = 1.0 g

Instance 2 *If a mole were defined to be* 3.00×10^{24} (*instead of Avogadro's number*), *what would be the mass of one mole of Argon atoms? Atomic weight of* Ar *on conventional scale is* 40.

Explanation From the given atomic weight, gram atomic weight of Ar is 40 g/mol on conventional scale.

⇒ 6.023×10^{23} atoms of Ar weigh 40 g

∴ 3.00×10^{24} atoms of Ar will weigh

$$\frac{40}{6.023 \times 10^{23}} \times 3.00 \times 10^{24} = 199.23 \text{ g}$$

$$\approx 199 \text{ g/mol}$$

Instance 3 *If the atomic mass unit "u" were defined to be one fifth of the mass of an atom of* C-12 *isotope, what would be the atomic weight of nitrogen in u, on this scale? Atomic weight of N on conventional scale is* 14.

Explanation This problem relates now, to change of conventional scale defining atomic weight in u unit. Let us consider w_1 to be the absolute weight of an atom of C-12-isotope and w_2 be the absolute weight of an atom of nitrogen. Also, let us consider "***A***" be the atomic weight of nitrogen in u unit, on changed scale. Now,

$$14 = \frac{w_2 \times 12}{w_1} \text{ u}$$

and

$$A = \frac{w_2 \times 5}{w_1} \text{ u}$$

[Change of scale will not alter the absolute atomic weight]

Taking ratio of above two expressions of atomic weight gives:

$$A = \frac{5 \times 14}{12} = 5.83 \text{ u}$$

Instance 4 *If* 80 g *of X combines with* 1.5×10^{23} *atoms of Y to form* X_2Y *without any of either element remaining, determine gram atomic weight of X.*

Explanation Given the molecular formula of compound to be X_2Y it indicates that an atom of Y combines with two atoms of X to form one molecule of X_2Y. From the given numerical information:

∵ 1.5×10^{23} atoms of Y combines with 80 g of X.

∴ 6.023×10^{23} atoms of Y (one mole) will combine with

$$\frac{80 \times 6.023 \times 10^{23}}{1.5 \times 10^{23}} = 321.23 \text{ g of } X.$$

Also, from formula "X_2Y", one mole of Y combines with two moles of X. Therefore, two moles of X weigh 321.23 g.

$\Rightarrow$ One mole of X will weigh

$$\frac{321.23}{2.00} = 160.615 \text{ g}$$

$$\simeq 160.62 \text{ g}$$

Instance 5 *If m atoms of X weigh 15 g and 4m atoms of element Z whose atomic weight is 30 u, weigh 45 g, determine the atomic weight of X.*

Explanation Number of moles of Z in its 45 g $= \frac{45}{30} = 1.5$

$\Rightarrow$ 1.5 moles of Z $= 4\,m$ atoms of Z

$\therefore$ 1.0 mole of Z $= 4\,m \times \frac{2}{3}\,m$ atoms of $Z = \frac{8}{3}\,m$ atoms

$\Rightarrow$ 1.0 moles of $X = \frac{8}{3}\,m$ atoms of X

$\because$ m atoms of X weigh 15 g

$\Rightarrow$ $\frac{8}{3}\,m$ atoms of X will weigh $\frac{15}{m} \times \frac{8}{3}\,m = 40$ g

Therefore, atomic weight of X = 40 u.

Fractional atomic weight

Most of the naturally occurring elements consist of their different isotopic forms, present in various proportions. Although each of the isotopic species has integral mass number, the average of the mass of various isotopes in the particular proportions often comes out as a fraction. This is the reason why atomic weight of many of the natural elements is fractional.

Instance 6 *Ordinary chlorine is a mixture of two isotopes* Cl-35 *and* Cl-37 *and their relative abundance is* 75% *and* 25% *respectively. Calculate the atomic weight of ordinary chlorine.*

Explanation The atomic weight of chlorine

$$= \frac{35 \times 75 + 37 \times 25}{100} = 35.5$$

Instance 7 *Naturally occurring boron consists of two isotopes whose atomic weights are* 10.01 *and* 11.01. *The atomic weight of natural boron is* 10.81. *Calculate the relative isotopic abundance.*

Explanation Let the boron sample contain x per cent of isotope whose atomic mass is 10.01 u.

$\Rightarrow$ Percentage of other isotope $= 100 - x$

Average atomic weight

$$= 10.81 = \frac{x \times 10.01 + (100 - x) \times 11.01}{100}$$

$\Rightarrow$ $x = 19.8\%$ and other isotope is 80.2 %.

Molecules and the Molecular Theory of Matter

Material particles may be of two type viz. the atoms or the molecules. Atoms are ultimate indivisible particles of matter, but they are not capable of existing in free state and generally don't possess the same properties as the matter that is composed of them. Exceptions occur in the case of Nobel gases as He, Ne, Ar, Kr and Xe exist in free atomic states. Molecules are the smallest particles, which are capable of independent existence with all the relevant properties of matter. Molecules are made up of two or more atoms and the properties of a substance are the properties of its molecules.

Molecular weight (MW)

Like atomic weight, molecular weight of a substance is defined as

Molecular Weight

$$= \frac{\text{Weight of one molecule of the substance}}{\frac{1}{12^{\text{th}}} \text{ Part by weight of an atom of C-12 isotope}}$$

The molecular weight of a substance is defined as a number which denotes how many times a molecule of the substance is heavier than $1/12^{\text{th}}$ part by weight of an atom of C-12 isotope.

Gram molecular weight The gram molecular weight of a substance is the weight in gram of its 6.023×10^{23} molecules taken together.

Molecular weight of a compound Molecular weight of a compound is the total sum of the atomic weight of the constituent elements *e.g.*,

(i) H_2O (water)

MW = 2 × atomic weight of H + atomic weight of O

= 2 + 16 = 18

(ii) H_2SO_4 (Sulphuric acid)

MW = 2 × atomic weight of H + atomic weight of S + 4 × atomic weight of O = 2 × 1 + 32 + 4 × 16 = 98

(iii) $KCl \cdot MgCl_2 \cdot 6H_2O$ (Carnallite)

MW = atomic weight of K + atomic weight of Cl + atomic weight of Mg + 2 × atomic weight of Cl + 6 × molecular weight of H_2O = 39 + 35.5 + 24 + 2 × 35.5 + 6 ×18 = 277.5

(iv) $K_2SO_4Al_2(SO_4)_3 \cdot 24H_2O$ (Potash alum)

MW = 2 × 39 + 32 + 4 × 16+2 × 27+3(32 +64) + 24 × 18 = 948.

Instance 8 *Magnesium is the only metallic element present in chlorophyll. Analysis of a sample of chlorophyll revealed that it contains* 0.04% *of metal. Determine the minimum possible molar mass of Chlorophyll.*

Explanation For minimum molar mass, it is assumed that there is one Mg atom per molecule of chlorophyll. Therefore, one mole of chlorophyll must contain at least one mole of Mg atoms.

$$\Rightarrow \quad \text{molar mass of chlorophyll} \times \frac{0.04}{100} = 24$$

$$\Rightarrow \quad \text{molar mass of chlorophyll} = \frac{24 \times 100}{0.04}$$

$$= 6 \times 10^4 \text{ u}$$

Instance 9 *A sample of protein was analyzed for metal content and analysis revealed that it contained magnesium and titanium in equal amount (by weight). If these are the only metallic species present in the protein and it contains 0.015% metals by weight, determine the minimum possible molar mass of this protein.* [M: Mg = 24, Ti = 48]

Explanation Since the two metals are in equal amount by weight,
$$\frac{W_{Mg}}{W_{Ti}} = \frac{n_{Mg} \times 24}{n_{Ti} \times 48} = 1$$

$$\Rightarrow \quad n_{Mg} = 2n_{Ti}$$

Also, in a molecule of protein, the number of atoms of Mg and Ti must be a whole number. For minimum possible molar mass, a molecule of protein must contain minimum number of atoms of metals. Therefore, every molecule of protein contains at least one Ti and two Mg atoms.

$\Rightarrow$ One mole of protein must contain at least one moles of Ti and two mole of Mg atoms.

$\Rightarrow$ Weight of metals per mole of protein

$$= 48 + 2 \times 24 = 96$$

This 96 g of metal is the 0.015% of the minimum molar mass of protein.

$$\text{Hence, molar mass of protein} = \frac{96 \times 100}{0.015} = 6.4 \times 10^5 \text{ u}$$

Instance 10 *A plant virus is found to consist of uniform cylinderical particles of 150 Å in diameter and 5000 Å long. The specific volume of the virus is 0.75 cm³/g. If the virus is considered to be a single particle, find its molecular weight.*

Explanation Volume of virus

$$= \pi r^2 l = \frac{22}{7} \times \frac{150}{2} \times \frac{150}{2} \times 10^{-16} \times 5000 \times 10^{-8} \text{ cm}^3$$

$$= 0.884 \times 10^{-16} \text{ cm}^3$$

$$\therefore \quad \text{Weight of one virus} = 0.884 \times 10^{-16} \div 0.75 \text{ g}$$

$$= 1.178 \times 10^{-16} \text{ g.}$$

$$\therefore \quad \text{Mol. wt of virus} = 1.178 \times 10^{-16} \times 6.023 \times 10^{23}$$

$$= 7.059 \times 10^7 \text{ g/mol}$$

Instance 11 *From 200 mg of* CO_2, 10^{21} *molecules are removed. How many gram and moles are left?*

Explanation 6.023×10^{23} molecules of CO_2 = 44 g.

$$\Rightarrow \quad 10^{21} \text{ molecules} = \frac{44 \times 10^{21}}{6.023 \times 10^{23}}$$

$$= 7.31 \times 10^{-2} = 73.1 \text{ mg}$$

CO_2 left = 200 − 73.1 = 126.9 mg and mole of CO_2 left

$$= \frac{wt}{MW} = \frac{126.9 \times 10^{-3}}{44} = 2.88 \times 10^{-3}$$

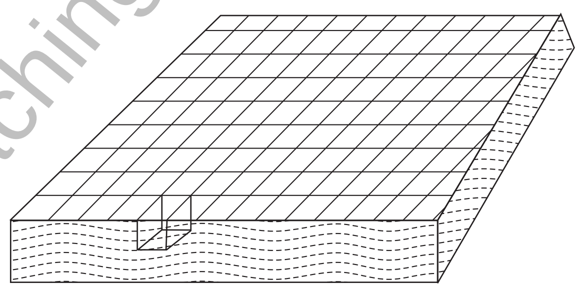
Instance 12 *Benzamin Franklin, a great scientist of his time performed a simple experiment for measurement of the extent to which oil spreads on water makes possible a simple estimate of molecular size and Avogadro's number. In a typical experiment, he spread* 4.00 cm³ *of an oil (molecular mass* = 200 g *and density* = 0.90 g/cm³) *over a pond of area* 2000 m². *He assumed that the oil molecules are tiny cubes that pack closely together and form a layer only one molecule thick on the surface of pond water as shown below in the diagram:*

(a) *Determine the radius of a single oil molecule.*

(b) *Determine the Avogadro's number.*

(c) *Is the Avogadro's number determined in "b" in agreement with the actual value of ? If not, what do you think to be the main source of error?*

(d) *Recalculate Avogadro's number assuming that the oil molecules are tall rectangular boxes rather cubic, with two edges of equal length and the third edge four times the length of the other two. Also assume that the molecules stand on end in water.*



Cross-sectional view of a single tiny cube containing a spherical molecule

Explanation (a) Volume occupied by an oil drop (V) on the surface of water = Area (A) of a side of a cubic box of molecule times length of molecule. It is due to the reason that molecules form a monolayer on the surface. Also boxes are cubical, all sides are of equal length.

$$V = A \times l$$

If there are N molecules, surface area covered by N molecules = NA

$\Rightarrow$ Volumes occupied by N molecules are $= NAl$

$\Rightarrow 4 \text{ cm}^3 = NAl = 2 \times 10^7 \text{ cm}^2 l$. ($NA$ = surface area of pond)

$$\Rightarrow \quad l = 2 \times 10^{-7} \text{ cm.}$$

Radius of oil drop = $l/2$ = 10^{-7} cm = 1.0 nm.

(b) $$N = 4 \text{ cm}^3 / A \cdot l = 4 \text{ cm}^3 / l^3 \qquad (\because \; A = l^2)$$

$$= \frac{4 \text{ cm}^3}{(2 \times 10^{-7})^3} = 5 \times 10^{20}$$

Mass of oil (m) = vol. $\times$ density = $4\,cm^3 \times 0.9\ g/cm^3$

$= 3.6$ g

Also given is the molar mass of oil = 200 g

$\because$ 3.6 g of oil contain 5×10^{20} molecules

$\therefore$ 200 g oil would contain

$$\frac{5 \times 10^{20}}{3.6} \times 200 = 2.78 \times 10^{22} \text{ molecules}$$

$\Rightarrow$ Avogadro Number $= 2.78 \times 10^{22}$

(c) Avogadro's number determined in Q. (b) is not in good agreement with the actual Avogadro's number which is 6.023×10^{23}. The error in calculation might be due to the assumptions that

(i) the oil molecules are tiny cubes.

(ii) the oil layer is single molecular thickness.

(iii) the molecular mass of 200 for the oil.

(d) In case of rectangular box shaped molecules.

Volume of box = area $\times$ height = $A \times y$

Volume of oil = NAy ; N is number of molecules.

$$\Rightarrow \quad y = \frac{\text{vol. of oil}}{NA} = \frac{4\ cm^3}{2 \times 10^7\ cm^2} = 2 \times 10^{-7}\ cm$$

Also $A = x^2$ and $x = \frac{y}{4} = \frac{2 \times 10^{-7}}{4} = 5 \times 10^{-8}$ cm

$$\Rightarrow \quad A = x^2 = 2.5 \times 10^{-15}\ cm^2$$

$$\Rightarrow \quad N = \frac{\text{Total surface area}}{\text{Surface area of one box}}$$

$$= \frac{2 \times 10^7\ cm^2}{2.5 \times 10^{-15}\ cm^2}$$

$$= 8 \times 10^{21}$$

$\because$ 3.60 g of oil contains 8×10^{21} molecules

200 g of oil would contain

$$\frac{8 \times 10^{21}}{3.60} \times 200 = 4.45 \times 10^{23} \text{ molecules.}$$

Instance 13 *One drop of an oily liquid polymer of spherical shape (radius = 1.00 nm) is spilled into a bucket full of water. Bucket is uniform cylindrical with radius of 50.00 cm. If the liquid polymer spread on the entire surface of water making exactly a monolayer of polymer molecules, determine molar mass of liquid polymer. The density of polymer is 0.60 g/cm^3. Also 10 drops of liquid polymer are equivalent to 1.00 cm^3.*

Explanation Volume of liquid polymer spilled = 0.1 cm^3.

$\Rightarrow$ Mass of liquid polymer spilled = 0.06 g

Let us consider that each polymer molecule is enclosed in a cubical box and vertically these cubical boxes form a monolayer on the surface. Length of the cubical box would be 2nm(diameter of the spherical polymer molecule).

$\Rightarrow$ Surface area of a cubical box (a)

$$= (2 \times 10^{-7}\ cm)^2 = 4 \times 10^{-14}\ cm^2.$$

Also surface area of bucket

$$= \pi r^2 = 4.14\ (50\ cm)^2 = 7850\ cm^2.$$

$\Rightarrow$ Number of molecules (which is equal to number of boxes present at the surface)

$$= \frac{A}{a} = \frac{7850}{4 \times 10^{-4}} = 1.9625 \times 10^{17}$$

$\Rightarrow$ 1.9625×10^{17} molecules weigh 0.06 g

$\Rightarrow$ 1.00 mole (6.023×10^{23} molecules) will weigh

$$\frac{0.06}{1.9625 \times 10^{17}} \times 6.023 \times 10^{23} = 184143\ g$$

$\Rightarrow$ Molar mass of polymer = 184143 g

Intext Q. 1 *How the gram molecular weight of a substance will be affected if definition of atomic mass unit is changed from (1/12)th part to (1/6)th part by weigh of an atom of C-12?*

Answer It will remain unaffected becuase it is an absolute weight.

Intext Q. 2 *How gram molecular weight will change if value of a mole is changed from* 6.023×10^{23} *to* 6.023×10^{24}?

Answer It will increase by a factor of 10.

Laws of Chemical Combination

All compounds are results of chemical union of elements. In entering into chemical combination with one another to form compounds, elements obey certain well-defined rules regarding their relative amounts, so that the composition of any particular compound is fixed. These rules are known as the **"Laws of Chemical Combinations"**.

The law of indestructibility of matter or the conservation of mass

It states that "In any chemical reaction, the total mass of the products is equal to the total mass of reactants". This law is derived from natural law of indestructibility of matter, according to which matter can neither be created nor be destroyed, but it can only be changed from one form to another form.

Instance 14 *When H_2S gas is passed through a solution of copper chloride, copper sulphide is precipitated and HCl is formed in solution. How much quantity of H_2S in grams is to be passed through a solution containing 13.4 g of copper chloride, so that 9.5 g of copper sulphide is precipitated and 7.3 g of HCl is formed in solution?*

Explanation Applying law of indestructibility of matter *i.e.*, conservation of mass, let w be the mass of H_2S required.

Mass of reactant = w + 13.4

Mass of product = 9.5 + 7.3

Equating mass of reactant and mass of product,

$$w + 13.4 = 9.5 + 7.3 \Rightarrow \quad w = 3.4.$$

The law of definite (or constant) proportions

It states that "In forming a compound, elements combine with one another in a fixed and invariable proportions of their weights *i.e.*, if a pure *AB* is composed of *x* part by weight of *A* and *y* part by weight of *B*, by whatever procedure *AB* is prepared, it will always contain *A* and *B* in the weight ratio $x : y$.

Illustration *Water is composed of the elements hydrogen and oxygen. It is available from various sources such as sea, river and well, lake, spring etc or can be synthesized in laboratory by combining elements. Water obtained from this source, on analysis they all have same mass ratio of* H : O (= 1 : 8). *Similarly, NaCl obtained from various sources will have same mass ratio of* Na : Cl (= 23 : 35.5).

Instance 15 *'C' is a compound.* 30 g *of C on analysis, give* 10 g *of A and* 20 g *of B. If* 15 g *of A reacts with* 50 g *of B, what mass of C will be formed*?

Explanation As given, at 30 g of compound *C* contains 10 g of A and 20 g of *B* *i.e.*, the mass ratio of *A* : *B* in *C* is $10 : 20 = 1 : 2$. Now according to law of definite proportions 15 g of *A* will combine with 30 g of *B* forming 45 g of *C* and 20 g of *B* will be left unreacted.

Law of multiple proportions

Law of definite proportion doesn't work when more than one compound is produced from the reacting elements as in case of oxidation of copper : two oxides Cu_2O and CuO are produced and they have different proportions of Cu. In these cases 'Law of multiple proportions' works which states that " When two elements combine to form more than one different compounds, the different weight of one element that combine with a fixed weight of the other element bear a simple integral ratio to one another. Thus if two elements *A* and *B* combine to form, say, three different compounds, *X*, *Y* and *Z* in which a fixed weight of *A*, say '*a*' grams is found to combine with b_1, b_2 and b_3 g of *B* forming *X*, *Y* and *Z* respectively, then $b_1 : b_2 : b_3$ will be a simple whole number ratio *e.g.*, 1 : 2 : 3 or 1 : 2 : 4 etc.

Law of reciprocal proportions

This law states that the "two elements combine with each other in the same proportion by weights in which they separately combine with a fixed weight of a third element".

Illustration *Carbon forms compound methane* (CH_4), *with hydrogen in which 12 part by weight of carbon combines with 4 part by weight of hydrogen. Also carbon forms* CO_2 *with oxygen in which 12 parts by weight of carbon combines with 32 parts by weight of oxygen. Hydrogen also combines with oxygen to form water* (H_2O). *In water molecule 2 parts by weight of* H *is combining with 16 parts by weight of oxygen i.e., they are combining in 1:8 mass ratio. In the above two compounds the mass of carbon is fixed i.e.,,* 12 g *and this fixed mass is combining with 4 g of* H *and 32 g of oxygen i.e., is in* 1 : 8 *mass ratio which is same as ratio of mass of* H *and oxygen present in water, hence law of reciprocal proportions is verified.*

Intext Q. 1 *If 10 g of reactants are allowed to react, at the end, the sum of masses of products formed and reactants remaining unreacted will be still 10 g. This fact is in accordance with which law?*

Answer The law of conservation of mass.

Intext Q. 2 *What is the significance of stoichiometric coefficients of a balanced chemical reaction?*

Answer Stoichiometric coefficients of a balanced chemical reaction represent the molar relations in which reactants do combine or products are formed.

Intext Q. 3 *Hydrogen combines with oxygen to form* H_2O *and* H_2O_2 *under different conditions. With this example verify the law of multiple proportions.*

Answer $H_2O : MW = 2 + 16 = 18$

$\because$ 2g Hydrogen $\equiv$ 16 g Oxygen

$\therefore$ 1 g Hydrogen $\equiv$ 8 g Oxygen

$H_2O_2 : MW = 2 + 32 = 34$

$\because$ 2 g Hydrogen $\equiv$ 32 g Oxygen

$\therefore$ 1 g Hydrogen $\equiv$ 16 g Oxygen

Different weight of oxygen combining with same weight of hydrogen are in 1 : 2 weight ratio hence the law of multiple proportions is verified.

Empirical Formula and Its Determination

The empirical formula of a compound is its simplest formula, which is generally arrived at from the analytical data of its constituent elements. It shows the simplest integral ratio of the number of atoms of the constituent elements present in a molecule of a compound. For example (Table 1.2),

Table 1.3 Molecular and empirical formula

Compound	Molecular formula	Empirical formula
Ethane	C_2H_6	CH_3
Benzene	C_6H_6	CH
Propanoic acid	$C_3H_6O_2$	$C_3H_6O_2$
Persulphuric acid	$H_2S_2O_8$	HSO_4

Determination of empirical formula from percentage composition of constituent elements:

From the given percentage (by mass) of constituent elements in a compound their empirical formulae can be derived as let compound contain three elements *A*, *B* and *C* with their mass percentage m_1, m_2 and m_3. Construct a table as in (Table 1.3).

Table 1.4 General approach for determining empirical formula

Elements	A	B	C
Mass %	m_1	m_2	m_3
# No. of moles	m_1/M_A	m_2/M_B	m_3/M_C
*Simplest mol ratio (SR)	$\frac{m_1}{M_A} \times \frac{M_C}{m_3}$	$\frac{m_2}{M_B} \times \frac{M_C}{M_3}$	1
Converting into whole number	If the simple mole ratio calculated above is fractional, they are converted into simple whole numbers by multiplying with a smallest common factor.		
Empirical formula	Now the empirical formula is written by writing constituent elements with simple whole number calculated above as subscript.		

M_A, M_B and M_C are the molar masses of A, B and C, respectively.

* Simple mole ratio of elements is determined by dividing no. of moles calculated in step 2 by the smallest no. of mole.

(*In this case moles of C, m_3/M_C is considered to be smallest*).

Instance 16 *If* 1.181 g *of an unknown element X reacts with oxygen to form* 1.664 g *of compound* X_2O_3, *what is the atomic weight of element X?*

Explanation

Element	X	O
Weight (in g)	1.181	0.483
Moles	$\frac{1.181}{M}$	$\frac{0.483}{16}$

Where M is molar mass of X

From the given formula Moles

$$\left(\frac{X}{O}\right) = \frac{2}{3} = \frac{1.181}{M} \times \frac{16}{0.483}$$

$$\Rightarrow \quad M = \frac{1.181 \times 16 \times 3}{2 \times 0.483} = 58.68 \text{ u}$$

Instance 17 *If a pure compound is composed of* X_2Y_3 *molecules and consists of* 60% *X by weight, what is the atomic weight of Y in term of atomic weight of X?*

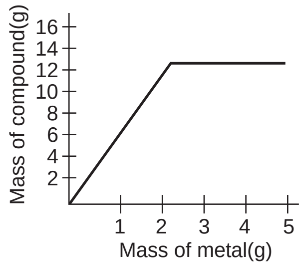
Explanation Let atomic weight of $X = M_x$ u, and of $Y = M_y$ u.

Element	% weight	% mole	Simple ratio	Stoichiometric ratio
X	60	$\frac{60}{M_x}$	1	2
Y	40	$\frac{40}{M_y}$	$\frac{40}{M_y} \times \frac{M_x}{60}$	$\frac{4M_x}{3M_y}$

$$\Rightarrow \quad \frac{4M_x}{3M_y} = 3;$$

Therefore, $$M_y = \frac{4}{9} M_x$$

Instance 18 *A series of experimental measurements were carried out with varying mass of a metal with a fixed mass of bromine. The adjacent graph shows the results. Empirical formula of the compound was found to be* MBr_3. *What is the approximate atomic weight of metal?*



Explanation

From the graph, it can be concluded that 13 g of compound is being produced from 2.25 (approximately) g of metal. Therefore, in a complete reaction 2.25 g of metal is combining with 10.75 g of bromine.

Element	Metal	Bromine
Mass	2.25	10.75
Mole	$\frac{2.25}{M}$	$\frac{10.75}{80}$
Simple ratio	1	$\frac{10.75}{80} \times \frac{M}{2.25} = 3$ $\Rightarrow M = 50.23$

Instance 19 *An organic compound has the percentage composition:* C = 26.09%, H = 4.35% *and* O = 69.5%. *Find the empirical formula of compound.*

Explanation Construct a table according as the given data.

Elements	C	H	O
% mass	26.09	4.35	69.56
No. of moles (Divide by their respective atomic masses)	$\frac{26.09}{12} = 2.17$	$\frac{4.35}{1} = 4.35$	$\frac{69.56}{16} = 4.35$
Simple ratio (Divide by smallest no. of moles)	1	$\frac{4.35}{2.17} = 2$	$\frac{4.35}{2.17} = 2$

So, the empirical formula is CH_2O_2.

Instance 20 *A crystalline hydrated salt on being rendered anhydrous, loses* 45.6% *of its weight. The percentage composition of anhydrous salt is* : Al = 10.5%, K = 15.1%, S = 24.8% *and* O = 49.6%. *Find the empirical formula of the anhydrous and crystalline salts.*

Explanation Let us first calculate the empirical formula of anhydrous salt as:

Elements	Al	K	S	O
% mass	10.5	15.1	24.8	49.6
No. of moles (Divide by their respective atomic masses)	$\frac{10.5}{27} = 0.39$	$\frac{15.1}{39} = 0.39$	$\frac{24.8}{32} = 0.78$	$\frac{49.6}{16} = 3.10$
Simple Ratio (Divide by smallest no. of moles)	1	1	2	8

So, the empirical formula of the anhydrous salt is $KAlS_2O_8$. The empirical formula weight is

$$1 \times 39 + 1 \times 27 + 2 \times 32 + 8 \times 16 = 258.$$

Now, the crystalline hydrated salt loses 45.6 % of weight on dehydration *i.e.*, 54.4 % is left as anhydrous salt.

$\because$ 54.4 g of salt combines with 45.6 g of water

$\therefore$ 258 g of salt combines with $\dfrac{45.6 \times 258}{54.4} = 216$ g of water.

Also molar mass of water is 18, no. of water molecules contained in one molecule of salt =216/18 = 12. Therefore, empirical formula of the crystalline salt is $KAlS_2O_8 \cdot 12H_2O$.

Instance 21 *A monobasic acid, containing nitrogen, hydrogen and oxygen only, gave the percentage composition by* weight as: N = 22.22%, H = 1.59%. *Determine the molecular formula of the acid.*

Explanation The percentage of oxygen in the acid is 100 – (22.22 + 1.59) = 76.19.

Construct a table for elucidating empirical formula first.

Elements	N	H	O
% mass	22.22	1.59	76.19
No. of moles	$\frac{22.22}{14} = 1.59$	$\frac{1.59}{1} = 1.59$	$\frac{76.19}{16} = 4.76$
Simple ratio	1	1	3

Therefore, empirical formula is HNO_3. Also the acid is monobasic, it contains one replaceable H. Thus, empirical formula is also molecular formula.

Instance 22 *One gram of a hydrated copper sulphate gave, on heating* 0.6393 g *of anhydrous salt. Calculate the number of molecules of water of crystallization per molecule of the hydrated salt.* [Cu = 63.5, S = 32]

Explanation Let the formula of hydrated salt be $CuSO_4 \cdot nH_2O$. On heating following reaction occurs:

$$\underset{\text{One mole}}{CuSO_4 \cdot nH_2O} \longrightarrow \underset{\text{One mole}}{CuSO_4} + \underset{n\text{-mole}}{nH_2O}$$

From the above reaction, it is obvious that one mole of anhydrous salt is obtained from one mole of the hydrated salt. Molecular weight of anhydrous salt is 159.5 (63.5 + 32 + 64).

Given, 0.6393 g of $CuSO_4$ is obtained from 1.0 g of hydrated salt.

$\therefore$ 159.5 g of $CuSO_4$ will be obtained from $\dfrac{1 \times 159.5}{0.6393} = 249.5$ g of hydrated salt.

$\therefore$ One mole of hydrated salt contain 249.5 – 159.5

= 90 g of water or 90/18 = 5 moles of water.

Thus, formula of the hydrated salt is $CuSO_4 \cdot 5H_2O$.

Instance 23 0.2012 g *of an organic compound, containing carbon, hydrogen and oxygen, gave on complete combustion,* 0.4431 g CO_2 *and* 0.1462 g *of water. The molecular weight of the compound is* 100. *Find out empirical and molecular formula.*

Explanation In the question, direct weight of element is not given. Therefore, first we calculate the weight of elements in compound from combustion data as:

44 g (mol. wt of CO_2) of CO_2 contains 12 g of C.

$\Rightarrow$ 0.4431g of CO_2 contains $\dfrac{12}{44} \times 0.4431$

$= 0.1208$ g of C.

Similarly 18 g of H_2O contains 2 g of H

$\Rightarrow$ 0.1462 g of H_2O contains $\dfrac{2}{18} \times 0.1462 = 0.0162$ g of H

$\Rightarrow$ Weight of "O" = 0.2012 – (0.1208 + 0.0162)

= 0.0642 g

Now construct a table, for determining empirical formula as

Elements	C	H	O
Mass	0.1208	0.0162	0.0642
No. of moles	$\frac{0.1208}{12} = 0.01$	0.0162	$\frac{0.0642}{16} = 0.004$
Simple ratio	$\frac{0.01}{0.004} = 2.5$	$\frac{0.0162}{0.004} = 4.05$	1
Convert into whole number	5	8	2

Thus empirical formula is $C_5H_8O_2$. Empirical formula weight is $5 \times 12 + 8 + 2 \times 16 = 100$, which is also the molecular weight. Therefore, molecular formula is same as empirical formula.

Intext Q. 1 *On what principle, does the empirical formula determination work?*

Answer The laws of definite proportions.

Intext Q. 2 *What is the relation between an empirical formula and molecular formula of the same compound?*

Answer Molecular formula = Empirical formula × n

Here, n = *a* whole number 1,2, 3 …

Intext Q. 3 *What will be the relationship in the empirical formulas calculated using different weights of the samples of a same compound?*

Answer It will be same in all determinations. In a given compound, atoms are present in fixed mass ratio irrespective to the mass of sample.

Calulations Based on Chemical Equations

An equation of a chemical reaction provides quantitative information relating the reactants and products involved in it. For quantitative relationship regarding masses or moles of reactants and products

involved in a chemical reaction, we first balance the given chemical reaction. Let us consider the following balanced generic reaction:

$$aA + bB \longrightarrow cC + dD$$

The above reaction describes a balanced chemical reaction and can be interpreted in term of moles as: 'a' mole of A combining with 'b' moles of B producing 'c' moles of C and 'd' moles of D. *e.g.*,

Molar interpretation

$$\underset{1}{C_2H_6} + \underset{3}{3XeF_6} \longrightarrow \underset{1}{C_2F_6} + \underset{6}{6HF} + \underset{3}{3XeF_2}$$

Hence, in the above reaction, reactants are combining in the molar ratio of

$$C_2H_6 : XeF_6 = 1 : 3$$

Depending on the type of reaction, we divide our calculation strategy into three categories:

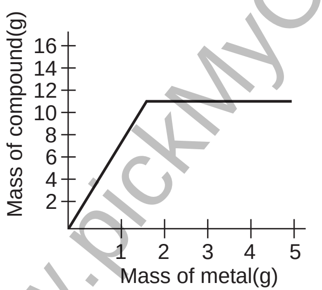
Problems based on mass-mass relationship

In this category we need to relate mass of reactants and products in a given chemical reaction. We first balance the chemical reaction and then interpret them in terms of moles and mass *e.g.*,

	$3BaCl_2$ +	$2Na_3PO_4$ $\longrightarrow$	$Ba_3(PO_4)_2$ +	$6NaCl$
Molar Interpretation	3	2	1	6
Mass Interpretation	$3 \times 208 = 624$	$2 \times 164 = 328$	601	$6 \times 58.5 = 351$

Hence in the above reaction, 624 g of $BaCl_2$ combines with 328 g of Na_3PO_4, and produces 601 g of $Ba_3(PO_4)_2$ and 351 g of NaCl.

Instance 24 *A weighed sample of a metal is added to liquid bromine and allowed to react completely. The product is then separated from any leftover reactants and weighed. The experiment is repeated with several masses of metals but with the same volume of bromine and results being plotted. If 20 g of each metal and bromine are allowed to react, determine the approximate weight of compound that will be formed.*



Explanation From the graph, it can be concluded that at the most 1.5 g (approximately) metal combines with 9.5 g of bromine (mass of compound is 11.00 g). In the given situation bromine is the limiting reagent. Therefore, mass of the compound formed from 20 g bromine $= \dfrac{11}{9.5} \times 20 = 23.15$ g.

Instance 25 *Four groups of students are studying the reactions of aqueous solution of alkali metal halides with aqueous solution of silver nitrate.*

Group A :	NaCl	*Group B :*	NaBr
Group C :	KCl	*Group D :*	KBr

If all the four groups dissolved 0.0040 *mol of their particular salt in some amount of water and treated with excess of* $AgNO_3$ *solution, which of the following statements is true concerning the above experiment?*

(*a*) *All the four groups will obtain same mass of precipitate.*

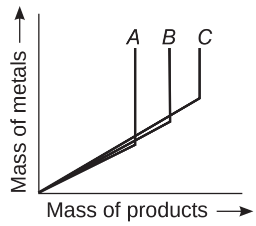
(*b*) *Group A and Group B will obtain the same mass of precipitate.*

(*c*) *Group C and Group D will obtain the same mass of precipitate.*

(*d*) *Group B and Group D will obtain the same mass of precipitate.*

Explanation Since every group is using same moles of halide, the pair of group having common halide will end up with same mass of AgX precipitate. In the present case and from the given options of combinations, Group B and Group D will end up with same mass of precipitate since they are using a common halide, bromide.

Instance 26 *Three metals of G II(A) elements were allowed to react with a fixed volume of liquid bromine separately and mass of metal bromides were plotted against mass of metals reacted as shown.*



From the plot relate the atomic weights of A, B and C.

Explanation Since mass of bromine is constant, same moles of metal bromide will be produced in each case. Also in this condition, the heaviest metal will produce maximum mass of product. Hence, the correct order of atomic weights of A, B and C is: $A < B < C$.

Instance 27 *Limestone* $(CaCO_3)$ *decomposes into quicklime* (CaO) *on strong heating. How much quantity of limestone will be required to prepare* 100 *kg of quicklime*?

Explanation The equation representing thermal decomposition of limestone is:

$$\underset{100\text{ g}}{CaCO_3} \longrightarrow \underset{56\text{ g}}{CaO} + \underset{44\text{ g}}{CO_2}$$

It is seen from the above equation that 56 g of quicklime is obtained from 100 g of limestone.

Therefore 100 kg of CaO from

$$\frac{100}{56} \times 100 \times 10^3 = 178.57 \times 10^3 \text{ g}$$

$$= 178.57 \text{ kg of limestone.}$$

Instance 28 *A specimen of hematite contains* 20% *of* Fe_2O_3. *What weight of iron can be obtained from one ton of hematite*?

Explanation Given, one ton of ore contains 20% *i.e.*, 0.2 ton of Fe_2O_3.

Also 160 g (MW of Fe_2O_3) of Fe_2O_3 contains 112 g of iron.

$\Rightarrow$ 0.2 ton of Fe_2O_3 will contain

$$\frac{112}{160} \times 0.2 = 0.14 \text{ ton of iron.}$$

Instance 29 6.0 g *of a sample of potassium chlorate* ($KClO_3$) gave 1.9 g of oxygen on strong heating. What is the percentage purity of the sample?

Explanation The balanced decomposition reaction is

$$\underset{122.5}{KClO_3} \longrightarrow \underset{74.5}{KCl} + \underset{48}{\frac{3}{2}O_2}$$

From the above equation, it is obvious that 48 g of oxygen is obtained from 122.5 g of potassium chlorate.

$\Rightarrow$ 1.9 g of oxygen will be obtained from

$$\frac{122.5}{48} \times 1.9 = 4.84 \text{ g of potassium chlorate.}$$

$$\Rightarrow \quad \% \text{ purity of sample} = \frac{4.84}{6} \times 100 = 80.8$$

Instance 30 5 g *of a sample of calcium carbonate* ($CaCO_3$) *contaminated with some volatile impurity left a residue of* 2.2 g *on strong heating. What is the percentage of pure* $CaCO_3$ *in the sample*?

Explanation Since impurity is volatile, the residue left after strong heating contains only pure CaO.

Mass interpretation of the decomposition reaction can be represented as

$$\underset{100}{CaCO_3} \longrightarrow \underset{56}{CaO} + \underset{44}{CO_2}$$

Now, 56 g of CaO is obtained from 100 g of $CaCO_3$.

$\Rightarrow$ 2.2 g of residue (CaO) will be obtained from

$$\frac{100 \times 2.2}{56} = 3.93 \text{ g of } CaCO_3.$$

$$\Rightarrow \quad \% \text{ Purity} = \frac{3.93}{5} \times 100 = 78.6$$

Instance 31 12.46 g *of a mixture of* MgO *and* $MgCO_3$ *on strong heating lost* 4.4 g *in weight. What is the composition of mixture*?

Explanation In the above-mentioned mixture, weight loss will be only due to decomposition of $MgCO_3$.

Mass interpretation of the decomposition reaction can be represented as

$$\underset{84}{MgCO_3} \longrightarrow \underset{40}{MgO} + \underset{44}{CO_2}$$

44 g of weight is lost for every 84 g of $MgCO_3$.

Therefore, 4.4 g of weight will be lost from 8.4 g of $MgCO_3$. Thus, the mixture contains 8.4 g of $MgCO_3$ and 4.06 g of MgO.

$$\Rightarrow \quad \% \text{ of MgO} = \frac{4.06}{12.46} \times 100 = 35.58$$

and $\quad \%$ of $MgCO_3 = 64.42$

Instance 32 *How much potassium chlorate must be heated to get as much oxygen as would be obtained from* 21.6 g *of mercuric oxide*?

Explanation The two required reactions can be represented as

$$KClO_3 \longrightarrow KCl + \frac{3}{2}O_2,$$

and

$$3HgO \longrightarrow 3Hg + \frac{3}{2}O_2$$

From the above two reactions, it is obvious that three moles of HgO is equivalent to one mole of $KClO_3$ with respect to formation of oxygen.

Now, moles of HgO present in 21.6 g of it $= \frac{21.6}{216} = 0.1$

$\Rightarrow$ 0.1/3 moles of $KClO_3$ will produce same amount of oxygen as was produced by 0.1 mole of HgO.

$\Rightarrow$ Mass of $KClO_3$ in 1/30 mole of it $= \frac{122.5}{30} = 4.08$ g.

Instance 33 *Find out the weight of* $CaCO_3$ *that must be decomposed to produce sufficient quantity of carbon dioxide to convert* 10.6 g *of* Na_2CO_3 *completely into* $NaHCO_3$.

Explanation The two reactions are

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$Na_2CO_3 + CO_2 + H_2O \longrightarrow 2NaHCO_3$$

From the above two reactions, it is obvious that one mole of CO_2 is produced from decomposition of one mole of $CaCO_3$ and one mole of CO_2 is needed for converting one mole of Na_2CO_3 into $NaHCO_3$. Thus in the above two reactions, one mole of $CaCO_3$ is equivalent to one mole of Na_2CO_3.

Now, moles of $Na_2CO_3 = \frac{10.6}{106} = 0.1$. Therefore, moles of $CaCO_3$ required will also be 0.1. Thus 10 g of $CaCO_3$ (0.1 mol) is the required amount.

Instance 34 *How much quantity of zinc will have to be reacted with excess of dilute* HCl *solution to produce sufficient hydrogen gas for completely reacting with the oxygen obtained by decomposing* 5.104 g *of potassium chlorate*?

Explanation The three reactions involved here are:

$$KClO_3 \longrightarrow KCl + \frac{3}{2}O_2$$

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$$

$$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$$

From the above reactions following relationship can be derived:

Moles of oxygen produced $= 1.5 \times$ moles of $KClO_3$

Moles of hydrogen produced = moles of Zn

Also 0.5 moles of oxygen combine with 1 mole of H_2

$\Rightarrow$ ($1.5 \times$ moles of $KClO_3$) moles of oxygen will combine with $2 \times (1.5 \times$ moles of $KClO_3)$ moles of hydrogen.

$\Rightarrow$ Moles of Zn $= 2 \times 1.5 \times \dfrac{5.105}{122.5} = 0.125$

$\Rightarrow$ Mass of Zn $= 0.125 \times 65.3 = 8.1625$ g.

Instance 35 *A mixture of cuprous oxide* (Cu_2O) *and cupric oxide* (CuO) *was found to contain 88% copper. Calculate the amount of each oxide in 2 g sample of the mixture.*

Explanation Let there be x g of CuO in 100 g of mixture. Therefore, there is $100 - x$ g of Cu_2O in 100 g of mixture.

Now, moles of Cu = moles of CuO + 2 x moles of Cu_2O

$$= \frac{x}{79.5} + 2 \times \frac{100 - x}{143}$$

$$\text{Mass of Cu} = \left[\frac{x}{79.5} + 2 \times \frac{100 - x}{143}\right] \times 63.5 = 88 \ (Given),$$

Solving for x gives; $x = 9$ g

$\Rightarrow$ 100 g of mixture contains 9 g of CuO and 91 g of Cu_2O.

Thus, 2 g of mixture will contain 0.18 g of CuO and 1.82 g of Cu_2O.

Instance 36 1.42 g *of a mixture of* $CaCO_3$ *and* $MgCO_3$ *were heated till no further loss in weight takes place. The residue left was weighed and found to be* 0.76 g. *Find the percentage composition of the mixture.*

Explanation Let the mixture contains x g of $CaCO_3$ and $1.42 - x$ g of $MgCO_3$.

The decomposition reactions are

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$MgCO_3 \longrightarrow MgO + CO_2$$

Thus, moles of CaO = Moles of $CaCO_3 = \dfrac{x}{100}$

$$\text{Mass of CaO} = \frac{x}{100} \times 56$$

Similarly, moles of MgO = Moles of $MgCO_3 = \dfrac{1.42 - x}{84}$

$$\text{Mass of MgO} = \frac{1.42 - x}{84} \times 40$$

Total mass of residue = Mass of CaO + Mass of MgO

$$= \frac{x}{100} \times 56 + \frac{1.42 - x}{84} \times 40 = 0.76$$

Solving for x gives; $x = 1.0$, therefore, 1.42 g of mixture contains 1.0 g of $CaCO_3$ and 0.42 g of $MgCO_3$.

$\Rightarrow$ % of $CaCO_3 = \dfrac{1 \times 100}{1.42} = 70.42$

and % of $MgCO_3 = 29.58$.

Instance 37 1.331 g *of a mixture of* KCl *and* NaCl *gave, on treatment with silver nitrate solution,* 2.876 g *of dry silver chloride. Find the percentage composition of mixture.*

Explanation This question is based on precipitation reaction *i.e.,* chloride is being estimated in the form of AgCl.

The reactions involved here are

$$AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$$

$$AgNO_3 + KCl \longrightarrow AgCl + KNO_3$$

Thus, moles of AgCl = moles of (NaCl + KCl). Now, let us assume that the mixture contains x g of NaCl, therefore, mass of KCl = $(1.331 - x)$ g.

In terms of mole,

$$\frac{x}{58.5} + \frac{(1.331 - x)}{74.5} = \frac{2.876}{143.5}$$

$\Rightarrow$ $x = 0.597$

$\Rightarrow$ Mass of KCl $= 1.331 - 0.597 = 0.734$ g.

$$\% \text{ of NaCl} = \frac{0.597}{1.331} \times 100 = 44.9,$$

and % of KCl = 55.1

Instance 38 *A* 1.85 g *sample of mixture of* $CuCl_2$ *and* $CuBr_2$ *was dissolved in water and mixed thoroughly with* 1.8 g *portion of* AgCl. *After reaction, the solid which now contains* AgCl *and* AgBr *was filtered, dried and weighed to be* 2.052 g. *What is the % by weight of* $CuBr_2$ *in the mixture?*

Tactical Thinking $CuCl_2$ on dissolving in water gives Cu^{2+} and Cl^- ions. Similarly $CuBr_2$ on dissolving in water gives Cu^{2+} and Br^- ions. On adding AgCl, the new precipitate formed contains AgCl as well as AgBr. It indicates that some AgCl has been converted into AgBr according to following reaction:

$$Br^- + AgCl \longrightarrow AgBr + Cl^-$$

Explanation Now let us assume weight of $CuBr_2$ in the mixture be x g.

$\Rightarrow$ Moles of $CuBr_2 = \dfrac{x}{223}$

Moles of Br^- ions present in solution

$$= 2\,x \text{ moles of } CuBr_2 = \frac{2x}{223}$$

$$\text{Moles of AgCl added} = \frac{1.8}{143.5}$$

Now moles of Ag in the new precipitate = Moles of (AgCl + AgBr)

Moles of AgBr = Moles of Br^- present in the solution $= \dfrac{2x}{223}$

Mass of AgBr in the new precipitate $= \dfrac{2x}{233} \times 188$

Now moles of AgCl in new precipitate = Moles of AgCl added – Moles of AgBr formed

$$= \frac{1.8}{143.5} - \frac{2x}{223}$$

$\Rightarrow$ Mass of AgCl in new precipitate

$$= \left[\frac{1.8}{143.5} - \frac{2x}{223}\right] \times 143.5$$

$\Rightarrow$ Total mass of new precipitate

$$= \frac{2x}{223} \times 188 + \left[\frac{1.8}{143.5} - \frac{2x}{223}\right] \times 143.5 = 2.052 \text{ (Given)}$$

Solving for x, we get $x = 0.6314$ g

$\Rightarrow$ % mass of $CuBr_2 = \dfrac{0.6314}{1.85} \times 100 \approx 34.2$

Instance 39 1.0 *g of a sample containing* NaCl, KCl *and some inert impurity is dissolved in excess of water and treated with excess of* $AgNO_3$ *solution. A* 2.0 g *precipitate of* AgCl *separate out. Also, the sample is 23% by mass in sodium. Determine mass percentage of* KCl *in the sample.*

Explanation Moles of AgCl = Moles of NaCl + Moles of KCl

$$= \frac{2}{143.5} = 0.014$$

Also, mass of Na = 0.23 g and Na is in the form of NaCl

$\Rightarrow$ Moles of Na = moles of NaCl $= \frac{0.23}{23} = 0.01$

$\Rightarrow$ Moles of KCl = 0.004

$\Rightarrow$ Mass of KCl = $0.004 \times 74.5 = 0.298$ g

$\Rightarrow$ Mass percentage of KCl = 29.8

Instance 40 A *one gram sample containing* $CaBr_2$, NaCl, *and some inert impurity is dissolved in enough water and treated with excess of aqueous silver nitrate solution where a mixed precipitate of* AgCl *and* AgBr *weighing* 1.94 g *was obtained . Precipitate was washed, dried and shaken with an aqueous solution of* NaBr *where all* AgCl *was converted into* AgBr. *The new precipitate which contains only* AgBr *now weighed to be* 2.4 g. *Determine mass percentage of* $CaBr_2$ *and* NaCl *in the original sample.*

Explanation The precipitate exchange reaction can be manipulated comfortably as follows

$$AgCl + Br^- \longrightarrow AgBr + Cl^-$$

Mass gain = 44.5

Mass gain in the given question is $2.4 - 1.94 = 0.46$ g.

$\because$ 44.5 g is the mass gain for 143.5 g (1.0 mole) AgCl

$\therefore$ 0.46 g will be the mass gain for

$$\frac{143.5}{44.5} \times 0.46 = 1.483 \text{ g AgCl}$$

$\Rightarrow$ Moles of NaCl = 10.45×10^{-3}

$\Rightarrow$ Also, mass of AgBr = $1.94 - 1.483 = 0.475$ g

$\Rightarrow$ Moles of $CaBr_2$ = half of the moles of AgBr $= 1.26 \times 10^{-3}$

$\Rightarrow$ Mass of NaCl $= 10.45 \times 10^{-3} \times 58.5 = 0.61$ g,

and mass percentage = 61.

$\Rightarrow$ Mass of $CaBr_2$ $= 1.2 \times 10^{-3} \times 200 = 0.24$,

and mass percentage = 24.

Limiting reagents in A chemical reaction

A reactant, which is less than the stoichiometric requirement, in a chemical reaction, is known as the limiting reagent and it is exhausted first. Let us consider a chemical reaction to understand concepts of limiting reagent:

$$Zn + S \longrightarrow ZnS$$

According to mole concept, one mole of Zn metal combines with one mole of S to produce one mole of ZnS. In term of mass, 65 g (atomic mass of Zn) of Zn combines with 32 g (atomic mass of S) of S to produce 97 g of ZnS *i.e.,* 32 g of sulphur is the stoichiometric requirement for complete reaction of 65 g of Zn to form ZnS.

Now let us consider that 20 g of S is mixed with 65 g of Zn and allowed to react according to the above mentioned reaction. Here S is less than stoichiometric requirement, which is 32 g. Thus, sulphur is the limiting reactant, will be consumed first, and some Zn will be left unreacted even at the end of reaction as: 32 g S reacts with 65 g of Zn.

$\Rightarrow$ 20 g of S will combine with $\frac{65}{32} \times 20 = 40.625$ g of Zn, and 24.375 g of Zn will remain at the end of reaction.

Working procedure in case of a limiting reagent

Once we come to know that one of the reagents is in limited amount, it is better to know which reagent is this before we attempt to determine the amount of product. Once it is known that which is the limiting reagent, amount of the product formed or amount of any other reactant consumed/left unreacted, can easily be determined from stoichiometry of the balanced chemical equation, with consideration that the limiting reagent is the only reactant going to be exhausted completely.

The next question is, how to know, which is the limiting reagent? This can be known very simply, as described below, depending on the units in which information regarding reactant is given. Usually reactants are provided with information of their moles or masses.

Case I *Reactants available with the information of their moles*

To understand this in a further simpler way, let us considers a chemical reaction involving formation of ammonia gas from the constituent elements. The balanced chemical reaction is

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

From the above balanced chemical reaction, it is evident that one mole of N_2 combines with three moles of hydrogen producing two moles of NH_3 gas, *i.e.,* stoichiometric ratio of H_2 to N_2 is 3. In any case,

if moles $\left(\frac{H_2}{N_2}\right) > 3$; H_2 is in excess or N_2 is the limiting reagent.

Or if moles $\left(\frac{H_2}{N_2}\right) < 3$; H_2 is the limiting reagent or N_2 is in excess.

Suppose in a given problem, 5.00 moles of nitrogen (N_2) and 12.00 moles of hydrogen (H_2) are available and the reactants combine to form ammonia (NH_3) gas as

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

Also, if it is stated that only 30% conversion is possible in the given reaction condition and that to with regard to

limiting reagent, how many moles of ammonia would be produced at the end of reaction? First, we calculate

$$\text{moles}\left(\frac{H_2}{N_2}\right) = \frac{12}{5} < 3$$

From the above calculations, it becomes evident that H_2 is the limiting reagent. Now, only 30% of the limiting reagent forms product.

$\Rightarrow$ $12 \times \frac{30}{100} = 3.6$ moles of H_2 will be consumed only.

Hence, moles of NH_3 produced will be

$$= \frac{2}{3} \times 3.6 = 2.4$$

Instance 41 *What weight of AgCl will be formed when a solution containing 4.77 g of NaCl is added to a solution of 5.77 g of $AgNO_3$?*

Explanation The chemical reaction occurring here is

$$NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3$$

Now, moles of NaCl given $= \frac{4.77}{58.5} = 0.0815$, and moles of $AgNO_3$

$$= \frac{5.77}{170} = 0.0339$$

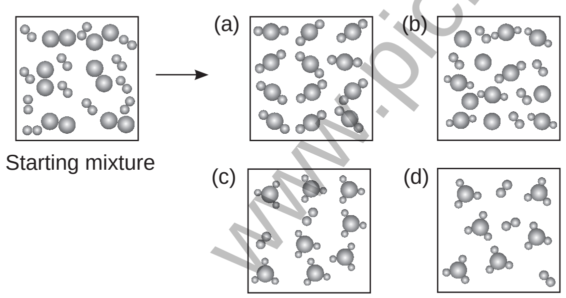
Here, $AgNO_3$ is the limiting reagent and moles of AgCl formed = moles of $AgNO_3$

$\Rightarrow$ Mass of AgCl $= 0.0339 \times$ mol. wt. of AgCl
$= 0.0339 \times 143.5 = 4.87$ g.

Instance 42 *Ammonia is formed in the direct reaction of nitrogen and hydrogen as*

$$N_2(g) + H_2(g) \longrightarrow NH_3(g)$$

The starting mixture is represented by the diagram in which the black (big) circle represents nitrogen and grey (small) circle represents hydrogen. Which of the following circle represents the product mixture?



Explanation The balanced chemical reaction is

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

In the starting mixture, there are six nitrogen molecules and twelve hydrogen molecules. Therefore, hydrogen is the limiting reagent in this case and at the end, there will be eight ammonia molecules and two nitrogen molecules will remain unreacted. Hence, option (c) is the correct one.

Instance 43 *Sulphur combines with oxygen to form two oxides SO_2 and SO_3. If 10 g of S is mixed with 12 g of O_2, what mass of SO_2 and SO_3 will be formed so that neither S nor oxygen will be left at the end of reaction?*

Explanation Moles of $S = \frac{10}{32} = 0.3125$,

and moles of $O_2 = \frac{12}{32} = 0.375$

Reactions involved in forming SO_2 and SO_3 are

$$S + O_2 \longrightarrow SO_2$$

and $$S + \frac{3}{2}O_2 \longrightarrow SO_3$$

Here, we will consider that first all S is converted into SO_2 and then SO_2 combines with unreacted oxygen to form SO_3 so that neither oxygen nor sulphur will be left at the end of reaction. Therefore, 0.3125 moles of S will combine with 0.3125 moles of O_2 to form 0.3125 moles of SO_2 and (0.375 – 0.3125) = 0.0625 moles of oxygen will be left unreacted.

Now: $$SO_2 + \frac{1}{2}O_2 \longrightarrow SO_3$$

i.e., one mole of O_2 combines with two moles of SO_2 to form 2 moles of SO_3.

$\Rightarrow$ 0.0625 moles of oxygen will combine with 0.125 moles of SO_2 to produce 0.125 moles of SO_3 and 0.1875 moles of SO_2 will be left unreacted.

$\Rightarrow$ Mass of $SO_2 = 0.1875 \times 64 = 12$ g and mass of SO_3
$= 0.125 \times 80 = 10$ g

Instance 44 *5.00 moles of hydrogen gas (H_2), 3.00 moles of white phosphorus {$P_4(s)$} and 12.00 moles of oxygen gas (O_2) are taken in a sealed flask and allowed to react as follows:*

$$H_2(g) + P_4(s) + O_2(g) \longrightarrow H_3PO_4$$

Determine the moles of ortho-phosphoric acid that can be produced, considering that the reaction occurs in 100% yield.

Explanation The balanced chemical equation for the formation of *ortho*-phosphoric acid is:

$$6H_2(g) + P_4(s) + 8O_2(g) \longrightarrow 4H_3PO_4$$

	H_2	P_4	O_2	H_3PO_4
Stoichiometric ratio:	6	1	8	4
Given moles:	5	3	12	0
Divide the given moles by three	$\frac{5}{3}$ (< 6)	1	4 (< 8); this relationship indicates that P_4 is in excess.	

In order to establish stoichiometric relations:

Multiply the above molar ratio by 2:	$\frac{10}{3}$ (< 6)	2	8

This relationship indicates that H_2 is the limiting reagent in the overall reaction. Hence, moles of H_3PO_4 will be determined from moles of hydrogen gas.

$$\text{Moles of } H_3PO_4 = \frac{4}{6} \times 5 = 3.33$$

Intext Q. 1 *In a chemical reaction involving two reactants, what will happen if both the reactants are the limiting reactants?*

Answer Both the reactants will be exhausted completely at the end.

Intext Q. 2 *In a chemical reaction, how one can establish the presence of a limiting reagent in a given mass of reactants?*

Answer If a reactant is left unreacted while other is exhausted completely, it is definitely a case of the presence of limiting reagent.

Intext Q. 3 *Let us consider the following reaction :*

$$A + 2B \longrightarrow C + D$$

If $\frac{w_A}{w_B} = 0.5$, *what conditions will make A limiting reagent and what other condition will make B a limiting reagent?*

Answer $$\frac{w_A}{w_B} = \frac{1}{2} = \frac{n_A M_A}{n_B M_B}$$

$$\Rightarrow \quad \frac{n_A}{n_B} = \left(\frac{M_B}{M_A}\right)\left(\frac{1}{2}\right)$$

If $\frac{M_B}{M_A} < 1$. A will be the limiting reagent otherwise B will be the limiting reagent.

Method of continuous variation

A more general approach to determine the limiting reagent is described here. This method, also called the **Method of Continuous Variation**, is a simple and effective approach for the determination of chemical reaction stoichiometry. Consider the following reaction :

$$aA + bB \longrightarrow dD \qquad \ldots (1.7)$$

which can be rewritten as follows (*by dividing all coefficients by "a"*) :

$$A + kB \longrightarrow mD \qquad \ldots (1.8)$$

where, $k = \frac{b}{a}$ and $m = \frac{d}{a}$. This method is based on the *fact*: *if a series of solutions is prepared, each containing the same total number of moles of A and B, but a different ratio, R, of moles B to moles A, the maximum amount of product, D, is obtained in the solution in which R = k (the stoichiometric ratio)*. To implement this method experimentally, let us prepare a series of solutions containing a fixed total number of moles of A and B, but in which the R is systematically varied from large to small, and measures the amount of product obtained in each solution. Then we plot amount of product versus R, and obtain a maximum at the initially unknown value of k.

That the maximum amount of product should occur at the stoichiometric ratio can be justified both intuitively and mathematically. The intuitive justification is : when R is greater than k, there is an excess of reagent B, so reagent A is the limiting reagent. As R is systematically decreased towards k (*i.e.*, as moles A increases and moles B decreases such that moles A + moles B stays constant) the amount of product increases with the amount of limiting reagent, A, until R becomes equal to k. In contrast, when R is less than k, there is an excess of reagent A, and B is limiting. As R is systematically increased towards k (*i.e.*, as moles of B increases and moles of A decreases), the amount of product increases with the amount of limiting reagent B, until R becomes = k. Putting this all together, we see that as R is varied over the range from zero to the maximum value investigated, the amount of product obtained increases until $R = k$, then decreases as R becomes larger than k. This demonstrates the method intuitively.

The mathematical justification is also quite simple. We use variable "x" to represent the moles of A in a particular solution, and assume that the total of the moles of A and B is to add 1.0 throughout the series of solutions. Then in each solution it will be true that

$$x = \text{moles } A$$

$$1 - x = \text{moles } B$$

Our goal is to show that the maximum amount of product is obtained when R = moles B/moles A = $(1 - x)/x$ is equal to k. We approach this by finding the value of x that maximizes product.

According to equation $A + kB \longrightarrow mD$, if x is less than the stoichiometrically correct amount of A, then A is limiting and moles of product = mx. A plot of moles of product *versus* x over a series of solutions should be linear, with slope m. Similarly, if x exceeds the stoichiometrically correct amount of A, then B is limiting and moles of product = $\frac{m(1-x)}{k}$. A plot of moles of product *versus* x over a series of solutions should also be linear, with slope = $-m/k$. The first plot will proceed up to the right as x increases. The second plot will proceed down to the right as x increases. At some point then, the two straight lines will intersect. At the intersection, they have a point in common. The value of x corresponding to this point is obtained by equating the ordinate values and solving for $x : mx = \frac{m(1-x)}{k}$

Solving, we get $x = \frac{1}{(1+k)}$.

Substituting in the expression for R, $\frac{(1-x)}{x}$, we find that the two lines intersect when

$$R = \frac{(1-x)}{x} = \frac{\left\{1 - \left[\frac{1}{(1+k)}\right]\right\}}{\left[\frac{1}{(1+k)}\right]} = k.$$

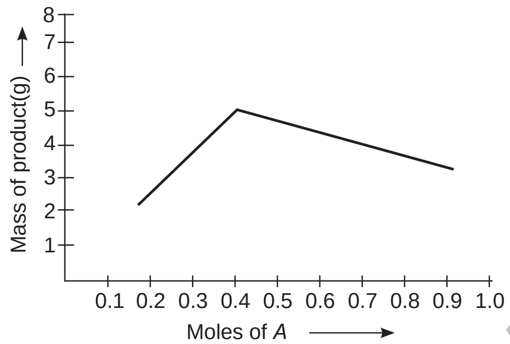
Because the amount of product increases as k is approached from either direction, the point of intersection of the lines occurs at the maximum amount of product obtainable. We have therefore shown that maximum product is obtained when $R = k$. This is what we set out to demonstrate.

Instance 45 *A and B are known to react to form D, but the stoichiometry is uncertain. Method of Continuous Variation yields the following data :*

Moles of A	Moles of B	Mass of product
0.2	1.8	2.50
0.3	1.7	3.75
0.4	1.6	5.00
0.6	1.4	4.38
0.8	1.2	3.75
1.0	1.0	3.12

Plot the quantity of products versus moles A to determine the stoichiometry.

Explanation

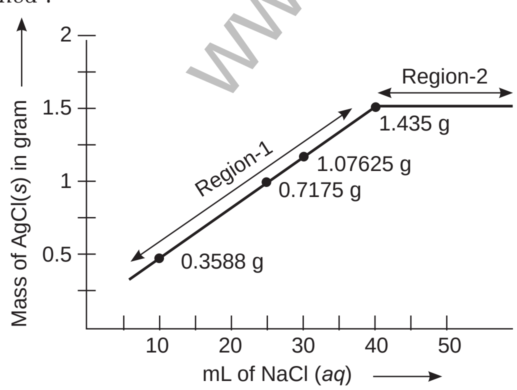


The plot as shown above. The value of k is clearly 4, because at the maximum, moles $\left(\frac{B}{A}\right) = \frac{1.6}{0.4} = 4$

Instance 46 $AgNO_3$ *and* NaCl *react in solution according to following reaction*:

$$AgNO_3(aq) + NaCl(aq) \longrightarrow AgCl(s) + NaNO_3(aq)$$

On reacting a fixed mass (1.70 g) *of* $AgNO_3$ *with varying volume of* 0.25 M *aqueous solution of* NaCl *and following plot is obtained* :



(a) *Why does the plot increases linearly in region-*1?

(b) *Why is the plot horizontal in region-*2?

(c) *What is the significance of the plot where the region-*1 *and region-*2 *lines meet (the breaking point)*?

(d) *Suppose you were to plot* $\left(\frac{NaCl}{AgNO_3}\right)$ *on X-axis. At what value of this quantity would the breaking point occur?*

(e) *If you were to use* KCl, *rather* NaCl *solution, but of the same strength, what would be the various plots look like?*

Explanation **(a)** In this region, the amount of product goes up linearly with the amount of NaCl added, because there is sufficient $AgNO_3$ in solution to react with all of the added NaCl. Reaction runs until the limiting reagent, NaCl, is gone. Region 1 defines the range in which NaCl is the *limiting reagent*.

(b) In region 2, the same amount of product is obtained no matter how much NaCl is added. Now the amount of product is determined by the fixed amount of $AgNO_3$ present in the solution. The same amount of product is always obtained because the amount of $AgNO_3$ is always the same. In region 2, $AgNO_3$ is the limiting reagent.

(c) The two lines intersect at the point where stoichiometrically equivalent amounts of NaCl and $AgNO_3$ are present. This gives the amount of NaCl that will exactly react with 1.700 g $AgNO_3$. When reaction is finished, both reactants will be gone. Neither reactant is the limiting.

(d) At the breaking point: moles $\left(\frac{NaCl}{AgNO_3}\right) = 1$ "Since equal moles of two reactants are combining"

(e) There will be no change in either X-coordinate or Y coordinate at breaking point since mass of $AgNO_3$ is same (1.7 g) and moles of $Cl^-(aq)$ will remain same even if we shift from NaCl to KCl but maintain the same molarity.

Problems Based on Mass-Volume Relationship

At NTP or STP (0°C and 760 mm of Hg.) one mole of any gas occupy 22.4 L. Also at any other different temperature and pressure, the relationship applicable to an ideal gas is: $pV = nRT$ where p is pressure, V is volume, n is number of moles, R is universal gas constant and T is absolute temperature.

Instance 47 *How much volume of sulphur dioxide at NTP will be obtained by completely burning* 10 g *of pure sulphur*?

Explanation The reaction involved is: $S + O_2 \longrightarrow SO_2$

i.e., one mole of S combines with one mole of O_2 to produce one mole of SO_2.

$$\text{Moles of S} = \frac{10}{32} = 0.3125$$

$$\Rightarrow \quad \text{Moles of } SO_2 = 0.3125$$

$$\Rightarrow \quad \text{Vol of } SO_2 = 0.3125 \times 22.4 = 7.0 \text{ L}$$

Instance 48 *A 10 g sample of* $KClO_3$*, gave on complete combustion, 2.24 L of oxygen at NTP. What is the percentage purity of the sample of potassium chlorate?*

Explanation The decomposition reaction is

$$KClO_3 \longrightarrow KCl + \frac{3}{2} O_2$$

$\because$ 3/2 moles of O_2 is produced from one mole of $KClO_3$

$\therefore$ One mole of O_2 will be obtained from 2/3 mole of $KClO_3$.

$$\text{Moles of } O_2 \text{ produced} = 2.24/22.4 = 0.1$$

$$\Rightarrow \qquad \text{Moles of } KClO_3 = \frac{0.2}{3}$$

$$\text{Mass of } KClO_3 = \frac{0.2}{3} \times 122.5 = 8.16 \text{ g}$$

$$\Rightarrow \qquad \% \text{ of } KClO_3 = \frac{8.16}{10} \times 100 = 81.6$$

Instance 49 17.24 g *of liquid* C_6H_{14} *(hexane) is enclosed with* 3.80 moles *of* $O_2(g)$ *in a cylinder fitted with a piston. The initial temperature of the mixture is* 27°C, *and the external (outside) pressure on the piston is* 1.00 atm. *The hexane and oxygen are then caused to react according to the following equation*:

$$C_6H_{14}(l) + O_2(g) \longrightarrow CO_2(g) + H_2O(l)$$

All of the hexane is used up. The heat produced by the reaction causes the temperature to rise to 77°C. *The external pressure is maintained at* 1.00 atm.

(*a*) *Balance the equation.*
(*b*) *Calculate the initial volume of reactants in the cylinder : (Assume that liquid hexane occupies a negligible volume.)*
(*c*) *Calculate the final volume of products and left-over reactants in the cylinder. (Assume that liquid water occupies a negligible volume.)*

Explanation **(a)** The equation is balanced by placing 6 before CO_2, 7 before H_2O, and 19/2 before O_2. Fractions are then rationalized by multiplying 2. The result is

$$2C_6H_{14}(l) + 19O_2(g) \longrightarrow 12CO_2(g) + 14H_2O(l)$$

(b) Initial volume of gaseous reactants in the cylinder. We initially have only liquid hexane and gaseous O_2 in the cylinder. We can ignore the very small volume occupied by the hexane. We have 3.80 moles $O_2(g)$ at 27°C and a pressure of 1.00 atm. The ideal gas law gives us the volume:

$$V = \frac{nRT}{p}$$

$$= \frac{(3.80 \text{ moles})\ (0.08206 \text{ L-atm / K mol})\ (300 \text{ K})}{(1.00 \text{ atm})}$$

$$= 93.55 \text{ L}$$

(c) Initial amounts of both the reactants are specified; we must determine which is limiting. Oxygen is already expressed in moles, so all we need to do is to compute the moles of hexane.

$$\text{Moles of hexane} = \frac{17.24 \text{ g}}{86.178 \text{ g/mole}}$$

$$= 0.200 \text{ mol}$$

The balanced equation indicates that 19 moles of oxygen are needed for each 2 moles of hexane. For 0.200 moles of hexane, moles of O_2 = 0.200 moles of hexane × (19 moles of O_2/2 moles of hexane) = 1.900 moles oxygen. Much more than this is available; hexane is limiting. Conclusions thus far:

All hexane is used up; 1.900 moles O_2 is used up, therefore 1.900 moles O_2 is left over.

CO_2 and H_2O are formed; volume of H_2O can be ignored. To calculate the moles of CO_2 formed is simple:

Moles CO_2 = Moles of hexane × (12 Moles of CO_2/ 2 moles hexane) = 0.200 × 6 = 1.200 mol CO_2

The total amount of gas at the end of reaction is 1.200 moles of CO_2 + 1.900 moles of O_2 = 3.100 moles of the gas. The volume can be calculated from the ideal gas law, using $T = 77 + 273$, and $p = 1$ atm:

$$V = \frac{nRT}{p} = (3.1)(0.08206)(350)/1 = 89.0 \text{ L}$$

The piston moves slightly in during reaction.

Measuring Strength of A Solution

A *solution* is a mixture of pure substances that is homogeneous at the molecular level. That is, the molecules of the substances are intimately intermixed. A two component solution may contain solid-liquid, liquid-liquid or solid-solid components. In stoichiometry usually, one of the substances is a liquid, called the *solvent*. A relatively small amount of a second substance, usually a solid, is then dissolved in the liquid. The substance that dissolves is called the *solute*. A solution is obtained when table sugar is dissolved in water. Water is the solvent, and sugar is the solute. Solutions are extremely important in chemistry. Dissolving the reactants in a solvent carries out most chemical reactions, and some substances are sold commercially as solutions because they are unstable in pure form. The amount of solute per unit amount of solvent is called the concentration (*Strength*) of the solution. Strength of a solution is measured in various units of concentrations as molarity, molality, normality, mole fraction, percentage strength, parts per million strength (ppm) etc.

Molarity "*M*"

It is defined as moles of solute present in one litre of solution.

$$\Rightarrow \qquad M = \frac{n}{V}$$

Where, n = no. of moles of solute and V is the volume of solution in litre.

Illustration *(i) Let us dissolve* 60g *of pure crystals of* NaOH *in water and dilute the solution by adding more water to get* 5.00 L *of alkali solution.*

Molarity is the moles of solute calculated for 1.0 L of solution. Here, moles of solute $= \frac{60}{40} = \frac{3}{2}$ moles of NaOH.

$\because$ 5.00 L of above solution contains $\frac{3}{2}$ moles of dissolved NaOH.

$\therefore$ 1.00 L of the solution has $\frac{3}{2} \times \frac{1}{5} = 0.3$ moles of dissolved NaOH.

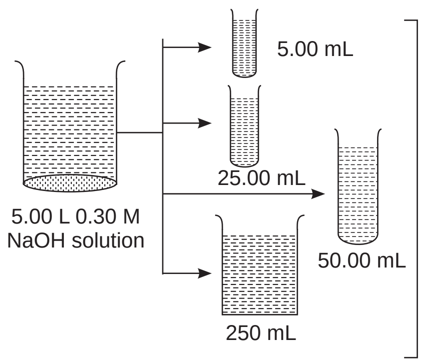
Hence, molarity of the above alkali solution "M" = 0.3 *i.e.*, the above solution is 0.30 molar.

Also, $M = \dfrac{\text{Moles of solute}}{\text{Volume of solution in litre}}$

$$= \frac{60}{40} \times \frac{1}{5} = 0.30 \text{ M}$$

Caution Point *Molarity is an "intensive quantity" i.e., it doesn't depend upon the amount of sample.*

In the above illustration, the molarity of alkali solution is 0.30 M. This indicate that, now if are to draw an aliquot of the above solution, its molarity would be 0.30 M irrespective of the volume of aliquot as:



Instance 50 *Determine mass of* $Na_2SO_4 \cdot 10H_2O$ *required for preparing* 250 mL *of salt solution whose molarity is* 0.45 *M.*

Explanation Given volume is 250 mL $= \frac{250}{1000}$ L = 0.25 L

$\Rightarrow$ Moles of hydrated salt required

$$= \text{Molarity} \times \text{Volume (in litre)}$$
$$= 0.45 \times 0.25 = 0.1125 \text{ moles.}$$

Molar mass of hydrated salt $Na_2SO_4 \cdot 10H_2O = 322$ g

$\Rightarrow$ Mass of salt required = Moles $\times$ Molar mass

$$= 0.1125 \times 322 = 36.225 \text{ g}$$

Instance 51 *A* 0.65M $BaCl_2$ *solution is prepared by dissolving pure solid* $BaCl_2 \cdot 2H_2O$ *in water. Determine the mass of hydrated salt dissolved per millilitre of solution and mass of anhydrous* $BaCl_2$ *present per millilitre of solution. Molar masses are* : Ba = 137, Cl = 35.5.

Explanation One millilitre of the solution $= 10^{-3}$ litre of solution.

$\Rightarrow$ Moles of hydrated salt required for 1.0 mL solution

$$= 0.65 \times 10^{-3}$$

$\Rightarrow$ Mass of hydrated salt required for 1.0 mL solution

$$= \text{Moles} \times \text{Molar mass}$$
$$= 0.65 \times 10^{-3} \times 244 = 0.1586 \text{ g}$$

Also, 1.00 moles of hydrated $BaCl_2 \cdot 2H_2O$ gives 1.00 moles of anhydrous $BaCl_2$ in solution:

Moles of anhydrous $BaCl_2$ per mL of solution

$$= 0.65 \times 10^{-3}$$

$\Rightarrow$ Mass of anhydrous $BaCl_2$ present in 1.0 mL solution

$$= 0.65 \times 10^{-3} \times 208$$

= 0.1352 g (208 is the molar mass of anhydrous $BaCl_2$).

Instance 52 *An aqueous solution is prepared by dissolving pure crystals of Mohr's salt* $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ *in water. Density of the above solution is* 1.2 g/mL *and the solution contains* 30% $FeSO_4(NH_4)_2 \cdot SO_4$ *by weight. Determine molarity of this solution and moles of the salt dissolved if the volume of solution is* 400 mL. *Molar masses* : Fe = 56, S = 32.

Explanation Since molarity is defined as moles of solute per litre of solution, it is always recommended to consider 1.0 L of solution to determine molarity when the density is given.

Therefore, mass of one litre of the above solution

$$= \text{volume} \times \text{density}$$
$$= 1000 \text{ mL} \times 1.2 \text{ g/mL} = 1200 \text{ g}$$

$\Rightarrow$ Mass of $FeSO_4(NH_4)_2SO_4$ present in 1.0 L of above solution

$$= \text{Mass of 1.0 L solution} \times \frac{30}{100} = 1200 \times \frac{30}{100} = 360 \text{ g}$$

$\Rightarrow$ Moles of $FeSO_4(NH_4)_2SO_4$ present in 1.0 L solution

$$= \frac{360}{284} = 1.268$$

$\Rightarrow$ Molarity (M) = 1.268 M

$\Rightarrow$ Also, $n = M \times V$

$\Rightarrow$ Moles of anhydrous salt in 400 mL solution

$$= 1.268 \times 0.40$$
$$= 0.5072$$

Moles of hydrated salt dissolved = Moles of the anhydrous salt in solution

Moles of hydrated salt dissolved for 400 mL solution = 0.5072

$\Rightarrow$ Mass of hydrated salt dissolved

$$= 0.5072 \times 392 = 198.82 \text{g}.$$

Instance 53 *Density of a sulphuric acid solution is* 1.2 g/mL *and it is* 40% H_2SO_4 *by weight. Determine molarity of this solution.*

Explanation Consider one litre of solution: Weight of solution = 1200 g;